

MOBILIZATION OF IRON IN PODZOL SOILS BY AQUEOUS LEAF EXTRACTS

SIR,—In a recent letter¹ Schnitzer has criticized the writer's views concerning the mechanism of the reaction between ferric oxide and aqueous leaf extracts; Schnitzer maintains that the process of mobilization is primarily one of peptization of the oxide by acidic polysaccharides.

In reply to these criticisms the following points are made. (1) DeLong and Schnitzer², in determining the "iron uptake capacity" of a leaf extract, apparently did not exclude atmospheric oxygen from the reaction vessel; reoxidation of any ferrous iron produced in the primary mobilization process would thus have been a distinct possibility. That reoxidation did take place is indicated by the facts that both ferrous and ferric iron were present in their final solutions, and that shaking the reaction mixture caused a decrease in the ferrous/ferric ratio of the mobilized iron.

(2) The evidence given by Schnitzer³ in support of his contention that dipyriddy gives erroneously high figures for the ferrous content of these reaction solutions could equally well be interpreted as indicating the formation of ferrous complexes of stability comparable to that of ferrous dipyriddy—such compounds have been shown to be formed by Scots pine needle extracts and ferrous iron⁴.

The writer's belief that there is a reduction stage in the reaction is based not only on the evidence of tests with dipyriddy, but also on the fact that for some 30 different tree species the amount of ferric oxide dissolved is decreased by allowing the reaction to proceed under aerobic conditions. Further, the decrease in the dipyriddy-reactive iron content, and the precipitation of iron compounds on aeration of anaerobically prepared reaction solutions is surely indicative of reoxidation. (See also ref. 5.)

(3) It is difficult to understand why Schnitzer considers that the fact that aluminium is dissolved, or otherwise mobilized, should argue against the possibility of ferric iron being reduced¹.

(4) On the basis of electrodialysis experiments Schnitzer has concluded that most of the mobilized iron is in colloidal form. Here again it seems that this could have been the result of reoxidation.

The writer has found that on dialysis through Cellophane, against two or three changes of distilled water, a freshly and anaerobically prepared Scots pine needle—iron solution lost 72% of its total iron content; the dialysate gave an immediate reaction for ferrous iron with dipyriddy. Oxidation of the original reaction solution decreased the proportion of dialysable iron.

(5) Schnitzer's observation that flavonal glycoside type compounds have little effect on ferric oxide is in agreement with the writer's experience. Such compounds represent a very small proportion of the

total polyphenols present in aqueous extracts of the fallen leaves of beech, oak, aspen, larch, etc., as well as of rimu and kuari. The largest proportion of the polyphenolic constituents consists of relatively high molecular weight compounds that appear to be present in the extracts at least partly in the form of salts; they are probably formed as the result of enzymic action in the fallen leaf.

Storage of undried leaves leads to an increase in the amount of the condensed polyphenolic compounds at the expense of the simpler phenols. Schnitzer's method of drying his leaves at room temperature is therefore likely to have favoured this process. Continued storage of the moist leaves apparently leads to such a degree of condensation of the polyphenols that they are no longer soluble in water, and at this stage the activity of the water extract falls off abruptly.

Leucoanthocyanins have been detected in some species and there are indications that, when present, these play a significant part in the reaction.

(6) Schnitzer and DeLong found an acidic polysaccharide in poplar leaves (*Populus grandifolia*) which possessed a considerable part of the activity of the original extracts⁶. More recently, however, MacLean and DeLong have shown that there is no correlation between the polysaccharide content of leaf extracts of several species and their "iron saturation capacities."⁷

The writer has found that the polysaccharide separated from aspen leaf extracts (*Populus tremula*) by the addition of alcohol is heavily contaminated with polyphenolic material. It is suggested that possibly it was this impurity that was responsible for the activity of Schnitzer's preparation since, after purification with charcoal the aspen leaf polysaccharide is quite without action on ferric oxide.

(7) Schnitzer observed that under his conditions increased iron mobilization was caused by increasing the pH of the reaction system. The writer has shown that aeration of a Scots pine needle—ferric oxide reaction solution leads to a more or less parallel decrease in the total and ferrous (i.e. dipyriddy-reactive) iron content of the solution at pH 4.3, but that at pH 7.6, while the ferrous content decreases considerably, the total iron remains nearly constant at its original value.⁴ This suggests the possibility that, in Schnitzer's experiments, increasing the pH prevented the precipitation of ferric compounds, and so caused an apparently greater mobilization.

(8) The writer has said that it is the fact that appreciable solution of ferric oxide takes place above pH 7, not, as Schnitzer says,¹ that the extent of solution is decreased by increasing pH, that indicates complex formation.⁸

(9) Finally, one might suggest that in Schnitzer's experiments, when the possibility of oxidation-reduction reactions taking place is being considered,

the choice of the nitrate as the ferric salt to use in "saturation capacity" determinations, and of nitric acid to adjust pH values was not a particularly happy one.

I am, Sir, etc.,

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References

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